INFLUENCE OF ZEOLITE NANOFILLERS ON PROPERTIES OF POLYMERIC MATERIALS

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ABSTRAKT: The present work deals with the preparation and study of modified polymeric materials with the replacement of carbon black by nanofillers on the basis of zeolite that is environmentally friendly. Natural zeolites from a group of aluminosilicate nanoporous materials have wide range of possibilities for applications that are environmentally friendly. Zeolites can be used in the role of fillers into the polymer materials too [1]. The given work deals with the preparation and study of modified polymeric materials with the substitution of carbon black by nanofillers on the basis of monoionic form - Ni(II) zeolite. The prepared monoinic forms – Ni(II) zeolite were characterized by the method of infrared spectroscopy. The vulcanization performance of prepared modified polymeric compounds and physical-mechanical properties of vulcanizates were measured and the efficiency of zeolite filler and carbon black filler was evaluated. The obtained values were compared with the values of commercially used polymer materials with the original composition.

Keywords: *Zeolite filler; carbon black; rubber compound; vulkanization performance; physical and mechanical properties.*

Introduction

The main priority in the rubber industry is production of environmentally friendly rubber compounds in the accordance with high quality of products and it means that the whole complex of problems relating to substitution of some substance with their ecological substituent is in the first position. Fillers belong to one of the important additives in the rubber compounds and carbon black is currently used in the function of filler in the common rubber compounds. Carbon black (Figure 1.) is a problematic substance because of its negative impact not only on environment but mainly on health of workers.

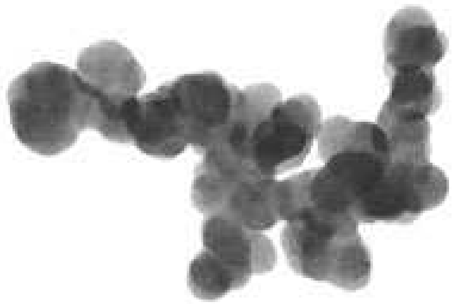

Figure 1. Electron microscope image of carbon black

This problem can be solved in the way of substitution of carbon black by some ecological additive. The application of inorganic materials in organic polymers is one of usual way to improve of mechanical properties including hardness, tensile strength and module of polymer materials [1].

Natural zeolites belong to the group of hydrated aluminosilicates with the porous structure (Figure 2.).

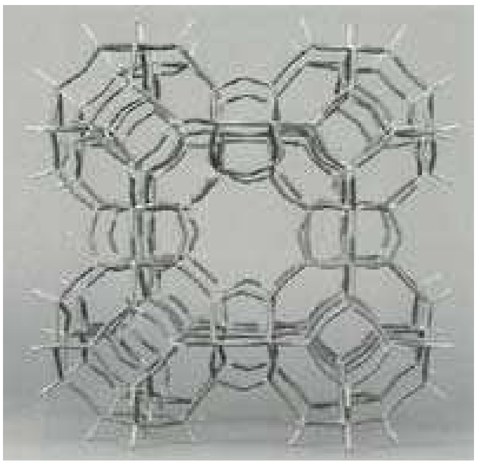

Figure 2. Structure of zeolite

Experiment

The natural zeolite clinoptilolite was used in a function of filler in rubber compounds. The model compounds were select on the basis of natural rubber (SMR) [2]. Carbon black (N660) was used as a comparative filler, because the size of its particles was approximately equalled to the size of particles of used natural zeolite.

The model rubber compounds were prepared by two-step of mixing in laboratory mixer called Plastograf-Brabender in the standard way. The first step of mixing was carried out at the temperature 90 °C and a rate of rotation pinions was 50 rpm/min. [4]. The activator of vulcanization (ZnO) together with the fillers carbon black and monioinc form - Ni(II) zeolites and the natural rubber were used for the preparation of modified rubber compounds. In the second step which was carried out at the temperature 90 °C and at the same rate, polymer sulphur in function of vulcanization agent (Sulphur N) and accelerator of vulcanization Rhenocure TP/S was added.

Table 1. Composition of modified model rubber compounds (samples 1, 2, 3) commercial rubber compound (R)

1. step				
Ingredient of compound	R	Sample 1	Sample 2	Sample 3
SMR 20 (g)	43	43	43	43
ZnO (g)	3.44	3.44	3.44	3.44
Stearic acid (g)	0.86	0.86	0.86	0.86
N 660 (g)	23.65	21.5	19.35	15.05
Zeolite Ni(II) (g)		2.15	4.3	8.6
2. step				
Sulphur N (g)	2.58	2.58	2.58	2.58
Rhenocure (g)	0.55	0.55	0.55	0.55

The composition of prepared modified rubber compounds is given in Table 1. Sample 1 – modified rubber compound with the substitution of 2.15 g of original filler by monoinic form – Ni(II) zeolites . Sample 2 – modified rubber compound with the substitution of 4.3 g of original filler by monoinic form – Ni(II) zeolites. Sample 3 - modified rubber compound with the substitution of 8.6 g of filler by monoinic form – Ni(II) zeolites. The prepared monoinic form – Ni(II) zeolite was analysed by the method of infrared spectroscopy.

The rubber compounds prepared at laboratory temperature had been left for 24 hours and then vulcanization curves were done by vulcameter MONSANTO 100 by STN 62 1416 at the temperature 150 °C during 60 min [5]. Rheological and vulcanization performances (M_L, M_H, t_S, t_{90}, R_V) of prepared rubber compounds with the addition of nanofiller clinoptilolite were investigated [6].

The determination of physical-mechanical properties of vulcanized rubber - stress-strain properties (tensile strength, modulus 300, tensibility) was done by instrument INSTRON at the temperature 23 ± 2 °C referring to STN ISO 37 [7]. Hardness was measured by hardness tester IRHD referring to ISO 48 at the temperature 23 ± 2 °C [8]. The evaluated values of prepared modified rubber compounds were compared with the values of commercial rubber compound.

Results and discussion

The results from determination of rheology and vulcanization performance of prepared rubber compounds are given in Table 2 and in Figures 3-4.

Table 2. Rheology and vulcanization performance of modified rubber compound (samples 1, 2, 3) and commercial rubber compound (R)

	R	1 sample	2 sample	3 sample
M_L [N.m]	12.8	10.7	10.2	15.9
M_H [N.m]	94.3	79.8	74.9	77.5
t_s [min]	1.8	1.5	1.8	2.0
t_{90} [min]	15	18.3	19.5	21.7
Rv [min^{-1}]	7.576	7.042	5.650	5.076

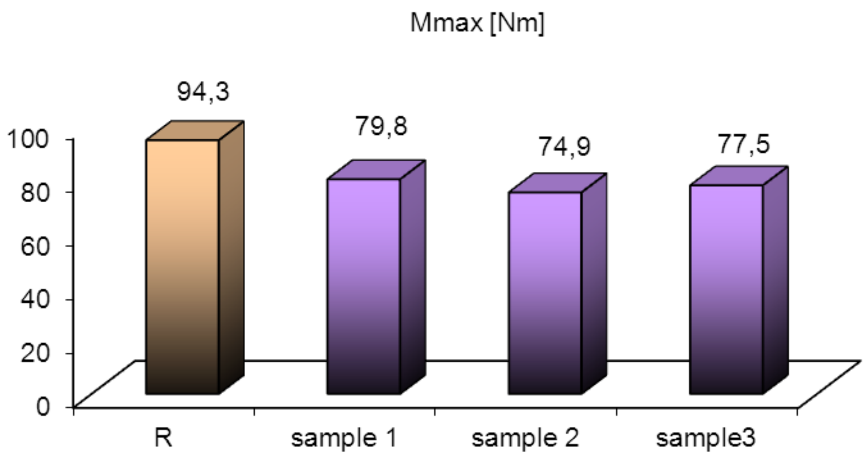

Figure 3. Maximal torgue moment M_H of model rubber compounds

The values of vulcanization performance confirmed that the used type of monionic form Ni(II) zeolite behaves as an inactive filler in comparison to carbon black (N660) in rubber compound. Viscosity decreases with increasing amount of used type zeolite in rubber compound (see a lower values of M_L and M_H (Fig. 3)) and there is also the elongation of optimal time of vulcanization (t_{90}).

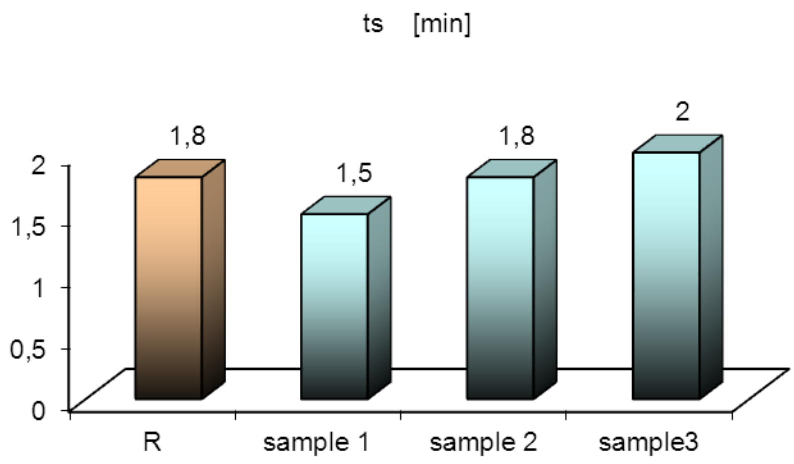

Figure 3. Scorch of time t_s of model rubber compounds

The scorch of time (t_S) is expressively higher in comparison to commercial rubber compounds R (Figure 3.) in the case of sample 3 where prepared monoionic form of zeolitic filler with weight 8.6g was added substituting carbon black. The values of rate coefficients (Rv) which characterize "activity" of ingredients in compound are the same as the values obtained for sample 2 and sample 3.

All vulcanization curves had the increasing "gradient" and it shows that the used natural zeolite is also partially „active filler". That can be caused by present of a little amount of oxides (mainly CaO and MgO). Both of these oxides can be used as activators of vulcanization too. Their content is very little in compound therefore the influence on vulcanization parameters is negligible. The given compound can also contain SiO_2 up to 70 % in natural zeolite and is connected with behavior to be the "inactive filler" which so called diluent in rubber compounds [3, 9].

The results of measurements of physical-mechanical properties of prepared vulcanizates are given in Table 3.

Table 3. Physical-mechanical properties of prepared vulcanizates

	R	Sample 1	Sample 2	Sample 3
Hardness [IRHD]	64.60	68.38	67.00	66.38
Tensile strength [MPa]	21.33	19.24	16.06	14.74
Tensibility [%]	355	275	288	299.8

The sample 1 where the 2.15 g of monoionic form - Ni(II) zeolite was used for substitution of carbon black shows the best values of physical-mechanical parameters. The sample shows the highest value of tensile strength and elongation at break too and it can be caused by relative synergic effect relating to combination of carbon black and natural zeolite.

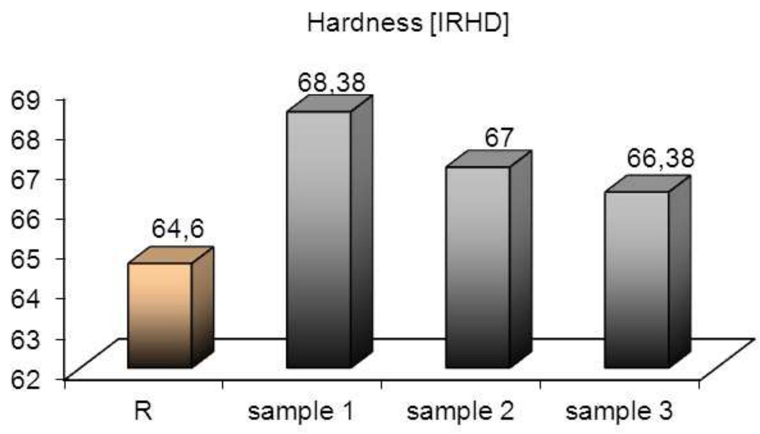

Figure 5. Hardness (IRHD) of vulcanizates

The hardness values of modified vulcanizates with zeolite filler (Figure 5) are a bit lower than the value of standard R containing only carbon black and it can be connected with lower „activity“ of used new prepared zeolitc filler in comparison to carbon black. The measured values of physical-mechanical parameters at sample 3 are not suitable from technological point of view.

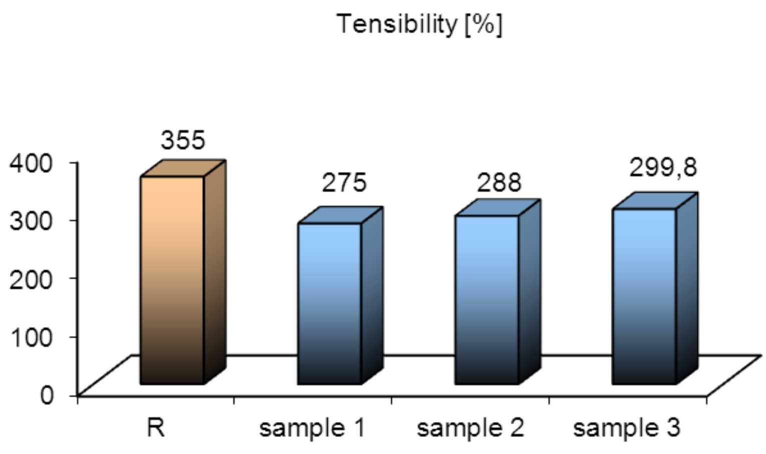

Figure 6. Tensibility of vulcanizates

The sample 3 shows a lower value of tensile strength to the prejudice of a high sensibility (Fig. 6) and it confirms the theory of high elasticity [9, 10] but complete substitution of carbon black by this type of natural zeolite is not possible because of available rubber technology. The used type of monoionic form – Ni(II) zeolite is „inactive filler“ in this case.

1.1. FTIR spectroscopy

The prepared monoionic form – Ni(II) zeolite was characterized by the method of infrared spectroscopy.

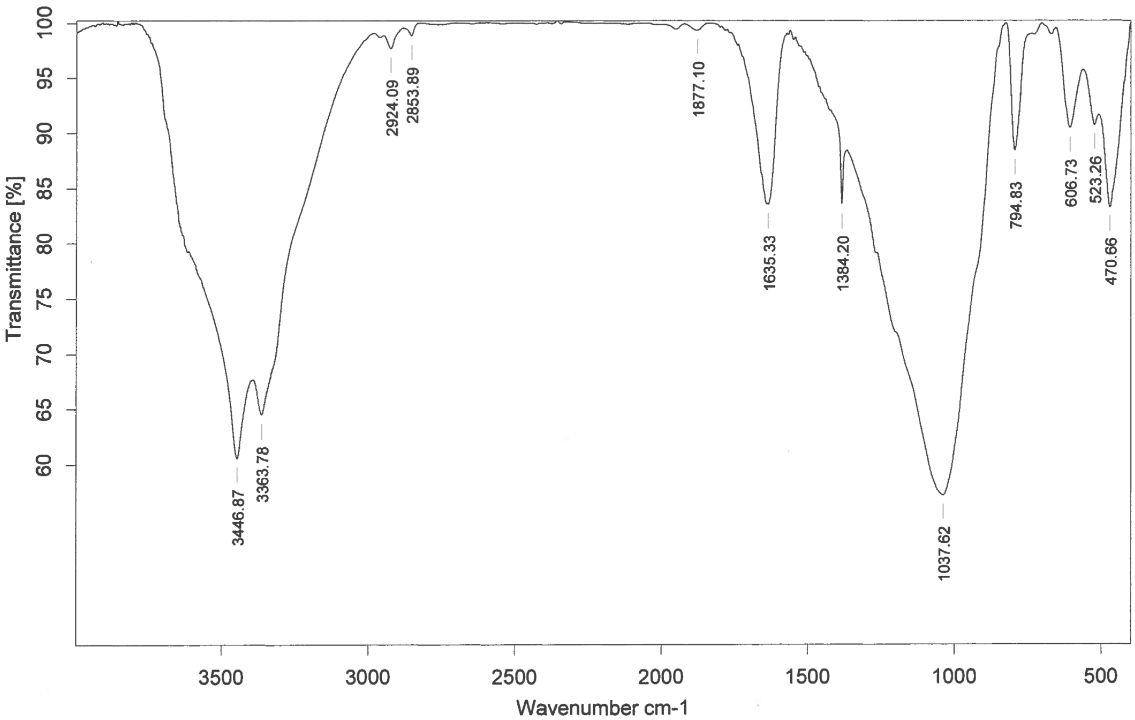

Figure 7. FTIR spectroscopy curve of nonionic form - Ni(II) zeolite

The IR spectra of the monoionic form - Ni(II) zeolite (Fig. 7) revealed several absorption bands in the studied region. For spectroscopic studies of zeolites is the most important medium infrared region, where there are absorption bands of fundamental vibrations of tetrahedrons [SiO4]4- and [AlO4]5- that may be attributed to two types of vibrations. The region from 1630 to 3690 cm-1 includs the absorption bands belonging to water contained in the zeolite cavities.

Infrared spectra of the investigated sample of zeolites were measured in the region of 4000 - 450 cm-1. The obtained absorption bands in the IR spectrum correspond to the following vibrations:

- Vibrations inside the tetrahedrons: 920 - 1250 cm-1 - asymmetric valence vibrations of tetrahedrons,650 to 720 cm-1 - symmetric valence vibrations of tetrahedrons, 420 to 500 cm-1 - deformation vibrations of tetrahedrons.
- Vibrations indicating character of bands between the tetrahedron and topology: 500 to 650 cm-1 - zeolites containing double 4 - and 6 - membered rings, 750 to

820 cm-1 - symmetrical valence vibrations of external bonds of tetrahedrons, 1050 - 1150 cm-1 - asymmetric valence vibrations of external bonds of tetrahedrons., 3440 cm-1 - a wide absorption band - symmetrical valence vibrations of OH groups, 1640 cm-1 - HOH deformation vibrations (iza-synthesis).

Conclusion

The rheological and vulcanization characteristics and physical-mechanical properties were studied for the prepared rubber compounds with modified composition which is environmentally friendly. Three models of rubber compounds were investigated where the carbon black N 660 as the reference filler was substituted by inorganic filler on the basis of zeolite.

According to study of modified rubber compounds, monoionic form zeolite - Ni(II) can be used as environmentally friendly filler for the application in the rubber compounds where especially physical-mechanical properties could be improved. The prepared rubber compounds will be studied and any other analysis will be confirmed by measured results.

Acknowledgements

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